Technical Reports 31 and 32

to the

OFFICE OF NAVAL RESEARCH

ARPA Order No. 26-60, Task 2, Item 3

Contract No.:   Nonr - 477 (16)

31. HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA
OF THE PENTAFLUOROSULFUR GROUP

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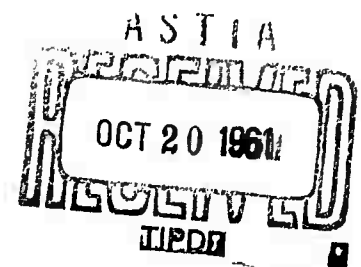32. NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME HYPOFLUORITES

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1961

High-Resolution Nuclear Magnetic Resonance Spectra

of the Pentafluorosulfur Group

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ABSTRACT

High-resolution NMR spectra have been obtained for a number of substances containing the pentafluorosulfur group ($-SF_5$). Because of a large coupling constant between fluorine atoms within this group, complex spin-spin interaction effects have been observed over a wide range of J/δ values. Line positions in these spectra are in excellent agreement with those calculated by the aid of an IBM 709 computer using an AB_4 or square pyramidal model for the fluorine atoms in the pentafluorosulfur group. Graphs are given representing the experimental and calculated spectra. In addition, there is presented a graphical method of estimating rather precisely the values of δ, J/δ, and line positions in the spectra of AB_4 NMR systems having J/δ values in the range 0.15 to 0.7.

Muller, Lauterbur, and Svatos[1] found that the NMR spectrum for the pentafluorosulfur group in various perfluoroalkyl derivatives of sulfur hexafluoride was more complex than would be expected for a first order spin-spin interaction between two types of fluorine atoms in a square pyramidal arrangement. The expected spectrum from simple considerations would consist of two multiplets, one a doublet with a separation of J (spin coupling constant) cycles per second and the other a quintet with a separation of J cps. The separation of the two multiplets would be the chemical shift, δ, between the two types of magnetically non-equivalent fluorine atoms. The above authors observed and explained, by calculation using the method of McConnell, McLean, and Reilly[2],

nine resonance frequencies for which the apex fluorine atom was responsible, and two broad resonance frequencies for which the fluorine atoms of the base of the square pyramid were responsible.

We have also observed for the AB_4 NMR system both in experimental and calculated spectra of $-SF_5$ derivatives nine distinct resonances due to the apex (or A) fluorine atom and we have found that each part of the doublet due to the four equivalent base (or B) atoms is further split into six "peaks" to give a total of twenty-one discrete resonance frequencies. The calculations of the NMR spectra for the AB_4 model were accomplished by the use of a generalized seven spin program written for the IBM 709 high speed digital computer.[3] The data obtained from this program were in the form of single frequency lines of computed intensity.

EXPERIMENTAL:

A Varian spectrometer Model 4311 B high-resolution NMR spectrometer employing a 40 Mc oscillator was used to acquire all of the spectra presented here. Samples for this study were placed in sealed five mm O.D. Pyrex tubing. Some caution had to be exercised in sealing and using the sample tubes because the internal standard, sulfur hexafluoride, can develop about twenty-five atmospheres vapor pressure at the temperature ($\sim 25^\circ C.$) that the spectra were taken.

DISCUSSION

In order to readily analyze an experimental NMR spectrum of an $-SF_5$ derivative, theoretical spectra were first computed for various values of the J/δ ratio using a constant value of J of

150 cps, which is nearly the correct value for J_{AB} for the
-SF$_5$ group. For J/δ ratios from 0.15 to 0.7 the line positions
were then plotted as a function of the ratio of J/δ. In order
to identify the lines and their positions, an arbitrary number-
ing system was set up, so that when all 21 lines were separate
the extreme line due to the apex (or A) fluorine atom was #1.
The others were numbered in increasing order in the direction
going toward the lines caused by the four equivalent (or B)
fluorine atoms. The sign of the chemical shift affected the
relative position of the A fluorine atom resonance with respect
to the resonance of the four B fluorine atoms. For a negative δ
the A fluorine atom resonance was at a lower field strength than
that of the B fluorine atoms. For a positive δ, the A fluorine
atom resonance was at a higher field strength than that of the
B fluorine atoms. When making computations the value zero on
the cycles per second scale was taken as the center of the reso-
nance "peaks" due to the four B fluorine atoms.

An examination of a theoretical, computed spectrum showed
that line #6 was the center of the A fluorine atom resonance. Its
computed position was equal to the value of the chemical shift,
δ, that was used in the computation. It was also found that lines
14 and 16, 12 and 17, 11 and 18, and 10 and 19 were symmetrically
positioned about the zero point. From this it followed that the

identification of any set or sets of these lines in an experimental spectrum readily gave zero on the scale. The identification of line #6 consequently gave the chemical shift.

The spin-spin coupling constant, J_{AB}, was not directly determinable from an experimental spectrum. From a set of computed spectra with J constant at 150 cps and with a variable δ such that J/δ ranged from 0.15 to 0.7, it was found that the ratio of the difference in cps between lines 8 and 10 and lines 6 and 10 was a fairly sensitive function of J/δ. Lines 6, 8, and 10 were also chosen because they were present with fairly large intensities. Using the computed data a plot of log (J/δ) .versus the ratio (line 8 to line 10)/(line 6 to line 10) gave a smooth curve. From this curve the value of J/δ for a compound could be determined from its experimental spectrum. See Figure 1. Since δ and the ratio J/δ could be found, J_{AB} was determined. Using these values of J and δ the spectrum of the compound was then computed. A close agreement between the computed and the experimental spectrum was considered to confirm the validity of the values of J and δ, and the basic model, AB_4.

A check in many cases on the value of J and δ was also made without computing a spectrum for the particular values, by comparison of the experimental spectrum with a spectrum plotted from graphs of the computed line positions as a function of J/δ. Figure 2 shows the line positions vs. the J/δ ratio, and Table I lists the data necessary to construct the graphs of Figure 2. Since the data for the graphical method of analysis were obtained for J = 150 cps,

the line positions as determined from the graphs for an experimental value of J/δ were corrected to the experimental value of J. This correction was accomplished by multiplying the line position by the factor of the experimental J divided by 150. For convenience the graphical representation in Figure 2 was built up using positive values for chemical shift with respect to the center of the complex doublet for which the four base fluorine atoms are responsible. If the experimental chemical shift was negative, it was necessary only to change the sign of the graphical values of the line positions in order to have agreement with the experimental spectrum and the sign convention of positive cps in the direction of increasing field strength.

When resonance frequencies appeared with displacements less than the resolution of the spectrometer, the experimental intensities appeared more or less as the sum of the individual resonances. For this reason some of the observed experimental lines in a spectrum corresponded to the sum of two or more lines. When experimental resolution was adequate to differentiate all of the resonance frequencies, the computed intensities of the lines agreed reasonably well with the experimentally observed intensities.

Other fluorine atoms in the molecule perturbed the resonance frequencies of the $-SF_5$ group with added splittings, but the basic line positions remained unaffected. Muller, Lauterbur, and Svatos[1] reported that the NMR spectra for $C_2F_5SF_5$, $C_3F_7SF_5$, and $C_4F_9SF_5$ did not show additional splitting due to interaction of fluorine atoms in the difluoromethylene group $(-CF_2-)$ with those of the $-SF_5$ group. We observed that in the spectrum of CF_3SF_5 all resonances of the

-SF$_5$ group were split into quartets by interaction of the fluorine atoms in the trifluoromethyl group (CF$_3$). The values for the coupling constants were 6.4 and 22 cps respectively between the fluorine atoms of the -CF$_3$ group and the A and B fluorine atoms attached to the sulfur atom. We also observed for C$_2$F$_5$OSF$_5$[8] that the interaction of the fluorine atoms of the -CF$_2$-group even though separated by an added oxygen atom was large enough to split all fluorine resonances of the -SF$_5$ group into triplets. The coupling constants were 3 and 10 cps respectively between the fluorine atoms of the -CF$_2$- group and the A and B fluorine atoms of the pentafluoro-sulfur group. However, it was also observed that for FCH$_2$CH$_2$OSF$_5$[8] the protons of the -CH$_2$- group did not interact sufficiently with the fluorine atoms of the -SF$_5$ group to cause any further splitting. Lack of resolution in the spectra of Muller, Lauterbur, and Svatos must have prevented the identification of the coupling constants between the fluorine atoms of the -CF$_2$- groups with those of the -SF$_5$ group.

Figure 3 shows the experimental NMR spectra of the compounds used in this study and gives the spin-spin coupling constants, chemical shifts, and spectra that were computed by use of experimental values. Superscripts following the chemical formulas of these compounds refer to the references giving the source of the compounds, method of preparation, or type of calculation of the computed spectrum.

Since the computer program used was inadequate for handling eight spin systems, the fluorine atoms of -CF$_3$ groups were in three instances (spectra III, XI, and XII) entered into computation as a single nuclear spin interaction. This six spin approximation

gave good correspondence between the major lines in the experimental quartets and the calculated doublets in the -SF_5 group resonances. Other calculated spectra that are given were computed as five spin systems.

Spectra XIII, XIV, and XV are very complicated spectra and appear to be examples of ten spin NMR systems. A five spin computation is given with spectrum XIII that shows the strong resemblance of the experimental spectrum to an AB_4 system.

The spin-spin coupling constants, J, in Table II are all remarkably constant; they fall close to the value 150 cycles per second, with a range of only twelve cycles. We believe this J should characterize all substituted SF_5 compounds, and probably even SF_6 itself. In a cis disubstituted compound, $SF_4(SO_3F)_2$[15], J was found to be 156 cycles. The value reported for another cis disubstituted compound, $\overline{CF_2CF_2OCF_2CF_2SF_4}$,[1] was only 93 cycles; however, the substitution forms a cyclic system, including the sulfur, and possibly causes changes in the SF_4 geometry. Further study of cis disubstituted compounds, and those with more substituents, should be interesting.

The chemical shifts, δ, listed in Table II are all referred to SF_6 as an internal standard. The δ values are for the most part negative; i.e., replacement of one fluorine in SF_6 by other halogen or oxygen causes the fluorine resonance to center about a lower value of magnetic field. Since the fluorine is replaced by a less electronegative atom, this should cause a decrease in the sulfur's effective electronegativity, and give a positive δ. The experimental evidence thus shows that electronegativity change is

certainly not the dominant factor, though it may be in CF_3SF_5 with a positive δ for the basal fluorine atoms. For the first two compounds, SF_5Br and SF_5Cl, the basal shifts are an order of magnitude larger than for any of the other compounds. This might then be due to the presence of low-lying excited electronic states, rather than changes in sp hybridization or double bond character.

For most of the remaining compounds certain regularities are apparent. The chemical shift for the basal fluorine atoms in the SF_5O- group with respect to fluorine in SF_6, whether bonded to sulfate, fluorosulfonate, pentafluorosulfur, perfluorocarbon, or perchlorofluorocarbon, usually falls around -15 ppm (though with a $-CF_3$ group it comes at -11.4 ppm). Glaring exceptions are found when SF_5O- is bonded to $-CH_2-$ and to SF_5O-. The former compounds might be explained by an electronegativity effect, but the apex fluorine shift is wrongly directed for this. The latter compound, the peroxy derivative, is practically unshifted from SF_6 itself in both basal and apex fluorines.

The chemical shifts of the apex fluorine are generally smaller in magnitude than the basal shifts. This is especially true of the first three compounds; the basal shifts extend over 106 ppm while the apex shifts cover only 0.55 ppm. The sulfate and fluorosulfonate are out of line to positive δ values, and the compounds containing the $-CH_2-$ group lie to larger negative δ values. It is apparent that further study of related compounds will be necessary before the origins of these shifts are understood.

ACKNOWLEDGEMENTS:

Table I

Line positions and intensities for AE$_4$ NMR model with varying J/δ values. J is a constant 150 cps and positions are measured with B$_4$ band center as zero.

Line no.	J/δ = 0.15 cycles	int.	J/δ = 0.18 cycles	int.	J/δ = 0.2236 cycles	int.	J/δ = 0.30 cycles	int.	J/δ = 0.40 cycles	int.	J/δ = 0.50 cycles	int.	J/δ = 0.70 cycles	int.
1	1318.10	0.57	1154.18	0.51	995.44	0.44	829.81	0.35	710.41	0.26	639.83	0.21	560.62	0.13
2	1198.62	0.67	1039.93	0.61	868.23	0.53	733.49	0.41	625.88	0.30	564.83	0.23	499.80	0.14
3	1160.37	2.21	995.55	2.08	835.79	1.90	668.94	1.62	548.75	1.34	477.92	1.16	399.01	0.78
4	1065.68	0.83	911.24	0.77	765.86	0.67	622.09	0.52	527.64	0.37	477.92	0.26	430.29	0.14
5	1022.37	2.81	860.11	2.73	704.10	2.60	543.94	2.33	432.46	1.95	370.04	1.59	306.25	1.03
6	1000.00	2.00	833.33	2.00	671.00	2.00	500.00	2.00	375.00	2.00	300.00	2.00	214.29	2.00
7	913.17	1.12	760.47	1.08	618.83	1.00	484.39	0.78	404.88	0.51	346.57	0.31	346.57	0.13
8	862.01	3.99	697.89	4.20	539.31	4.51	375.00	4.90	258.71	5.74	192.12	6.32	121.53	7.22
9	728.02	1.82	568.31	2.04	416.75	2.37	265.99	2.96	167.71	3.62	117.12	4.08	69.74	4.55
10	82.13	4.82	82.19	5.04	81.32	5.36	77.42	5.94	69.47	6.57	60.80	7.02	46.37	7.49
11	73.36	6.90	72.67	7.20	71.47	7.51	68.94	8.05	65.04	8.72	60.80	9.30	52.48	10.2
12	70.38	6.94	68.59	7.12	65.71	7.36	60.28	7.72	53.30	8.07	47.08	8.31	37.35	8.60
13	64.63	7.79	62.78	6.92	60.21	7.10	56.06	7.38	51.25	7.77	47.08	7.90	40.28	8.22
14	62.57	6.77	60.10	6.88	56.66	7.03	51.13	7.24	44.94	7.43	39.83	7.57	32.16	7.73
15	56.90	4.43	54.15	4.49	50.56	4.56	45.19	4.65	39.59	4.74	35.17	4.80	28.67	4.87
16	-62.57	3.57	-60.10	3.51	-56.66	3.44	-51.13	3.35	-44.94	3.26	-39.83	3.20	-32.16	3.13
17	-70.38	5.23	-68.59	5.12	-65.71	4.97	-60.28	4.75	-53.30	4.55	-47.08	4.42	-37.35	4.25
18	-73.36	5.21	-72.67	5.07	-71.47	5.09	-68.94	4.62	-65.04	4.32	-60.80	4.09	-52.48	3.75
19	-82.13	5.06	-82.19	4.88	-81.32	4.63	-77.42	4.26	-69.47	3.88	-60.80	3.61	-46.37	3.32
20	-87.01	5.01	-89.56	4.80	-93.31	4.59	-100.00	3.93	-108.71	3.28	-117.12	2.68	-132.24	1.78
21	-103.02	3.18	-109.98	2.96	-120.75	2.63	-140.99	2.04	-167.71	1.38	-192.12	0.92	-230.45	0.45

Table II

Chemical shift parameters, δ, in ppm, referred to internal SF_6, and spin-spin coupling constant, J, in cycles/sec, between apex and basal fluorine atoms.

Compound	basal F	apex F	J
SF_5Br	-88.2	-5.00	143.1
SF_5Cl	-68.4	-4.88	148.5
CF_3SF_5	18.4	-5.43	145.4
SF_5OSO_2F	-14.8	1.63	153.5
$(SF_5)_2SO_4$	-15.1	0.43	153.4
$FC_2H_4OSF_5$	-2.48	-17.98	153.8
$FClC_2H_3OSF_5$	-2.69	-15.93	154.7
$C_2F_5OSF_5$	-15.2	-3.35	152.8
$C_3F_9OSF_5$	-14.7	-4.00	154.9
$FC_2Cl_4OSF_5$	-14.8	-6.37	154.9
CF_3OSF_5	-11.4	-4.23	153.0
SF_5OSF_5	-14.0	-4.53	150
SF_5OOSF_5	0.75	0.16	

Figure 1. Determination of J/J' by ratio of B to IO distance to 6 to IO distance.
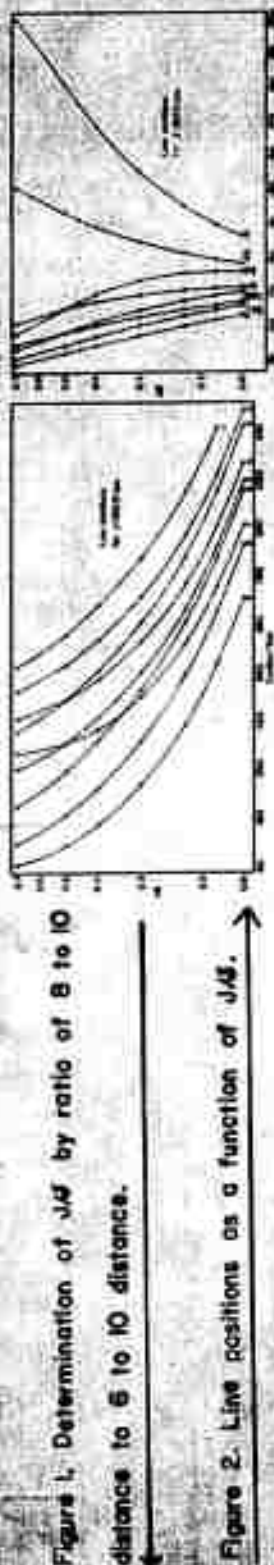
Figure 2. Line positions as a function of J/J'.
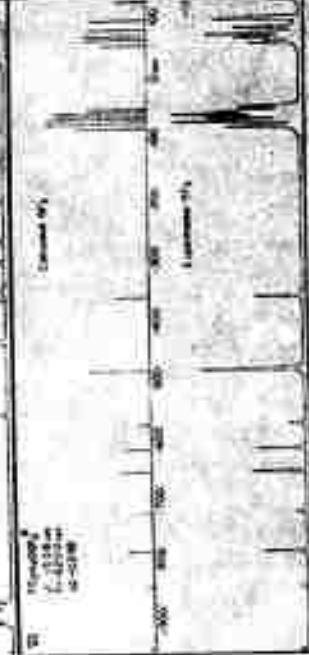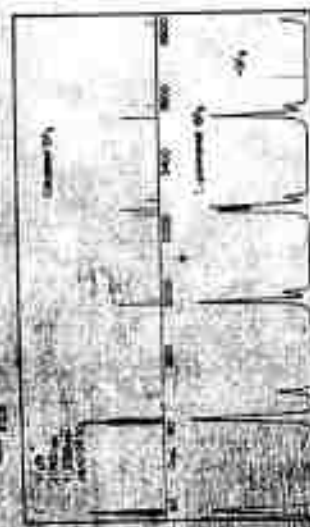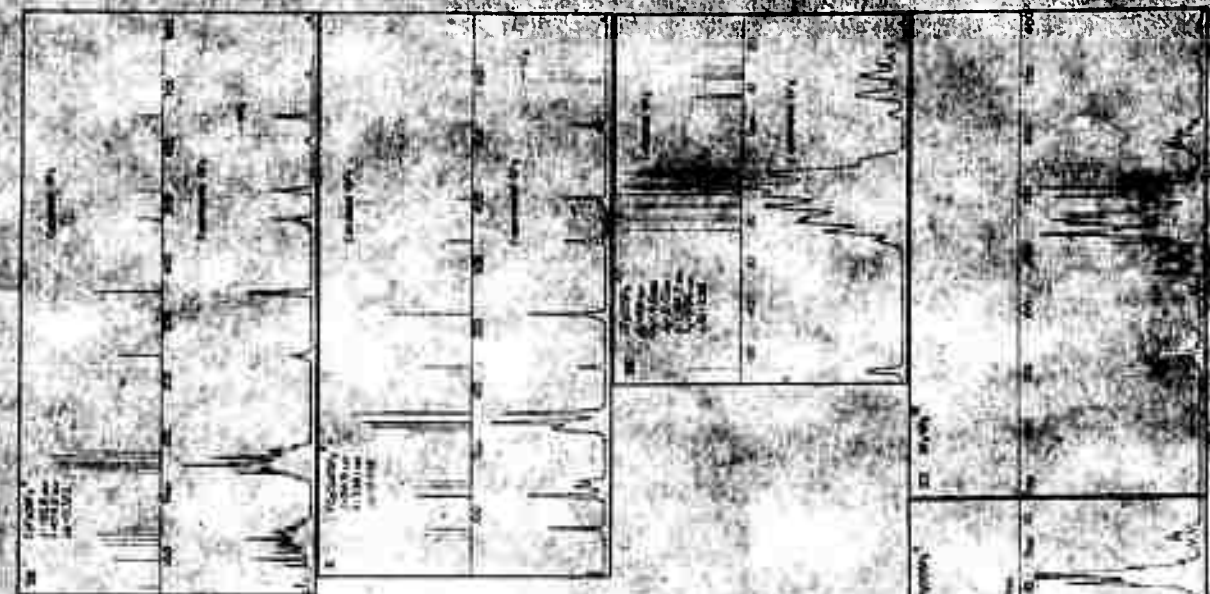
Figure 3. Experimental and calculated spectra.

Figure 3. (continued)

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Nuclear Magnetic Resonance Spectra of Some Hypofluorites

By Claude I. Merrill and George H. Cady

ABSTRACT

The nuclear magnetic resonance spectra of F_2, OF_2, SF_5OF, SO_3F_2, and CF_3OF have been observed at room temperature with SF_6 as an internal reference. Fluorine absorbs at lowest magnetic field strength while with increasing field absorption due to the hypofluorite fluorine atoms fall in the order given above. The NMR spectrum of SF_5OF is the only one exhibiting observable second order spin-spin interaction. Computation using an AB_4X model successfully explains the spectrum. This is consistent with a SF_5OF structure in which the $-SF_5$ group fluorine atoms are arranged in a square pyramid around the sulfur atom.

The NMR spectra of F_2, OF_2, CF_3OF, SF_5OF, SO_3F_2 were taken

to see how the hypofluorite resonances of the hypofluorites

compared with elemental fluorine and with each other. At the

same time it was desirable to observe coupling constants between

different types of fluorine atoms in the hypofluorites and to

gain additional information concerning molecular structure.

In Table I is presented the order into which the NMR reso-

nances of the hypofluorite fluorine atoms of the hypofluorites

fall along with the various coupling constants and chemical

shifts observed. Sulfur hexafluoride because of its ready avail-

ability and its ability to dissolve all substances mentioned

here was chosen as internal reference. The order given in Table

I is that which would be expected from electronegativity con-

siderations alone. It shows that the valence of fluorine in the

-OF group is not positive; instead the fluorine is somewhat

negative. The order of SF_5OF and SO_3F_2 is the reverse of
that previously reported,[1] but this is most likely due to the
fact that in the previous work the NMR spectra of these two
compounds were taken at different temperatures while in this
work the spectra were observed at a single temperature.

All spectra obtained in this work were simple and uncom-
plicated by second order spin-spin splittings except SF_5OF.
F_2 and OF_2 possessed single resonances, CF_3OF gave a large
doublet for the CF_3 group and a smaller quadruplet for the -OF
resonance as reported by Ogg,[2] and SO_3F_2 gave two equal-sized
doublets as reported before.[1] Previously, the spectrum of
SF_5OF was reported to consist of six resonances for the -OF
group and a doublet for the $-SF_5$ group and was considered to
indicate that the five fluorine atoms in the $-SF_5$ group were
magnetically equivalent.[1] With the higher resolution used in
the present research, a fine structure was obtained indicating
that the five fluorine atoms are not magnetically equivalent.
The spectrum is shown in Figure 1.

With the aid of a generalized seven-spin program[3] for the
IBM 709 high-speed digital computer a reasonable match between
the experimental spectrum of SF_5OF and a computed spectrum was
realized. The computation assumed a AB_4X spin system which
corresponds to a square pyramid orientation for the fluorines
of the $-SF_5$ group. The fact that one fluorine atom in the $-SF_5$
group was distinctly different from the other four invalidates

evidence for fluorine exchange within the -SF$_5$ group furnished by the previous study.[1] Table II gives both the experimental and computed NMR spectra of SF$_5$OF. Even the high resolution obtained in this study was insufficient to resolve all resonances in the SF$_5$OF spectrum. By grouping lines that are very close together the calculated spectrum is found to agree very well with the experimental spectrum.

EXPERIMENTAL:

Sample tubes were made from 5 mm Pyrex glass tubing of 1 mm wall thickness. Each tube was filled by condensing together sulfur hexafluoride and the substance to be studied. After the tube had been sealed hermetically it was tested for strength by placing it in water (in a hood) at 32°C. Some tubes exploded from pressure. Those which did not were used.

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(3) Program provided by Prof. K. B. Wiberg, University of Washington.

TABLE I

Chemical Shifts and Coupling Constants from

NMR Spectra at 40 Mc.

Substance	Chemical shift, δ, compared to SF_6 as zero (cycles per second)[a]		Spin-spin coupling constant, J (cps)		
	δ for F_2 or -OF	δ for SF or CF			
F_2	-14,620 cps				
OF_2	-8,680 cps			between	
SF_5OF	-5,250 cps	SF* 68.5 cps	(SF* and OF)		0.0
		SF_4 144.1 cps	(SF_4	OF)	17.4 cps
			(SF_4	SF)	155.0 cps
FSO_2OF	-4,850 cps	SF 558 cps	(SO_2F	OF)	6.1 cps
CF_3OF	-3,700 cps	CF_3 5,140 cps	(CF_3	OF)	33.2 cps

* apex fluorine atom resonance in $-SF_5$ group

[a] Values are positive in the direction of increased magnetic field strength.

TABLE II

Experimental and Calculated SF₅OF NMR Spectra at 40 Mc.[*]

experimental position	calculated position	relative intensity
5430.7 cps	5430.86 cps	0.987
5429.0	5428.30	0.988
5413.5	5416.10	0.992
	5413.43	2.982
5410.5	5409.71	2.982
	5408.10	0.995
5399.7	5401.61	0.998
	5399.77	2.994
5396.0	5396.00	4.000
5386.6	5387.50	1.003
	5387.42	3.004
	5387.41	1.003
	5387.27	3.005
5378.5	5378.63	3.021
5374.3	5373.94	1.008
5365.2	5366.02	1.011
5360.7	5361.26	1.013
SF₅ group		
75.6	75.60	4.000
35.7	35.63	8.827
30.2	30.21	11.810
27.7	27.13	8.888
	26.84	8.673
22.4	22.89	7.979
	21.88	8.981
	21.06	7.987
	20.36	4.994
18.0	17.86	11.934
13.6	13.47	8.763
7.9	11.46	4.939
	9.33	7.912
	7.77	8.910
	6.57	7.927
	5.60	4.958
-4.2	-3.74	3.030
	-4.51	4.043
	-5.46	3.037
-12.8	-12.84	3.117
-25.2	-23.94	3.016
	-25.20	4.028
	-26.82	3.029
-35.7	-35.28	3.147

[*] Values given here are positive in the direction of lower magnetic field. The planar fluorine atoms of the -SF₅ group are assigned zero chemical shift.
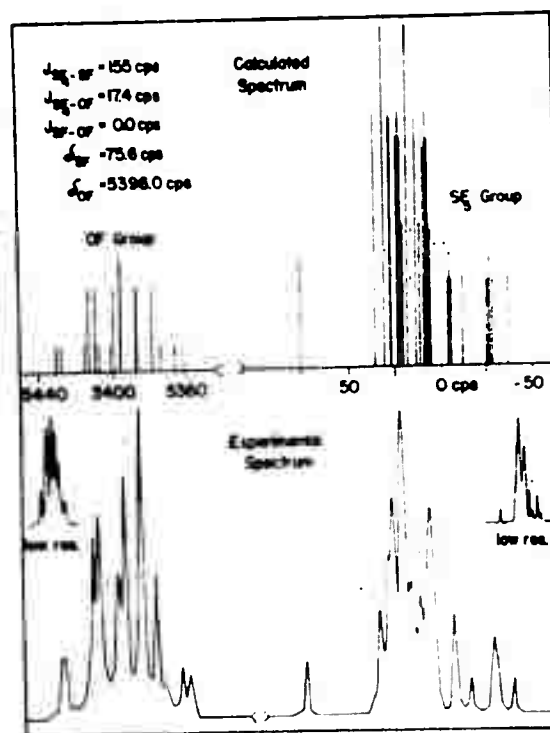
Figure 1. Spectrum of SF_5OF at 40 Mc. both experimentally and calculated. Low resolution parts of the spectrum are given on the left and right sides of the figure. Planar fluorines of $-SF_5$ group are given zero chemical shift.

UNCLASSIFIED